

DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review Electrolyzers For CO₂ Conversion from BioSources

April 7, 2023
Carbon Dioxide Utilization Session
Rich Masel,
Dioxide Materials

The Team



Electrolyzer scaling

- Rich Masel
- Zengcai Liu
- Daniel Carillo-Gomez
- Sunil Rajana
- Mohammed Mohammed
- Audrey Holland
- Luis Cerna-Berantes

Tech. Manager: Sonia Hammache

PM: Ryan Lawrence



Optimizing Selectivity

- K.C Neyerlin
- Danielle Henckel
- Mike Resch
- Andrew Young

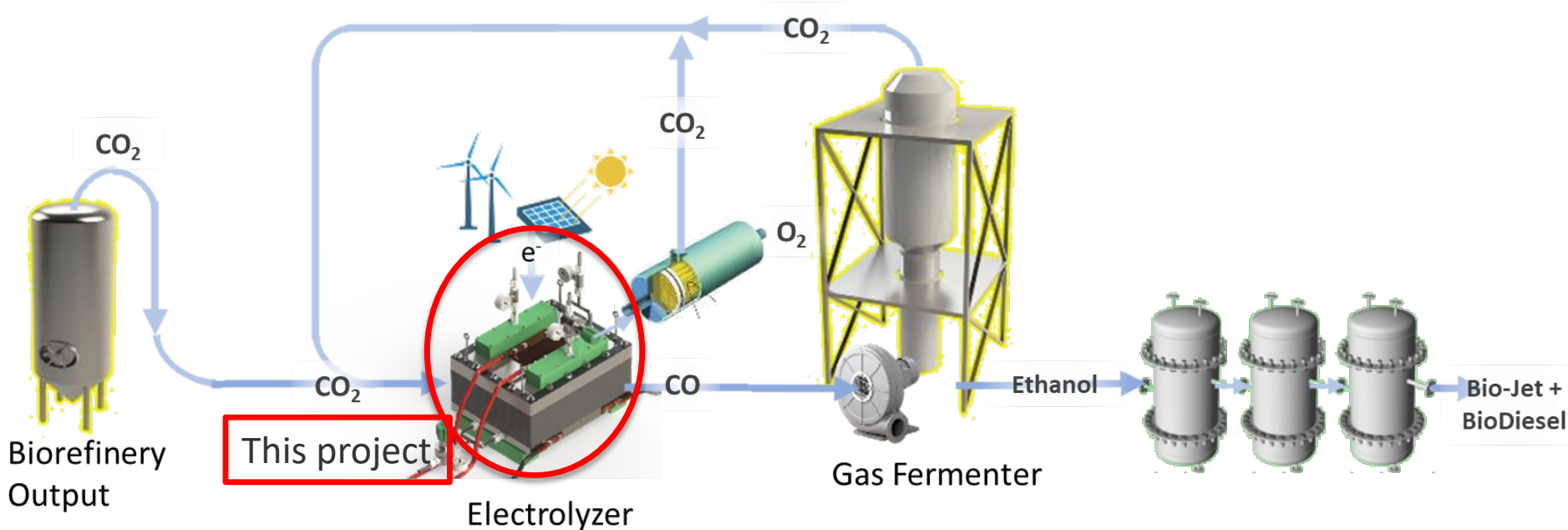


MicroCT

- Debbie Meyers

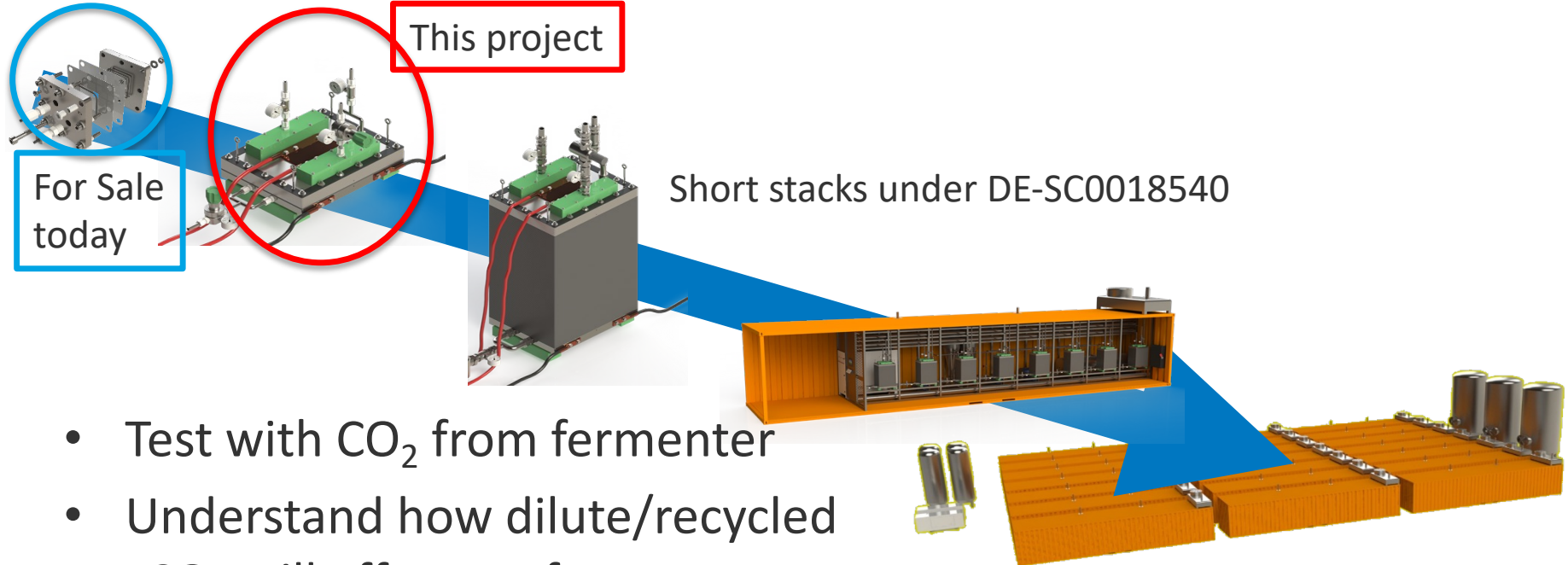
Project Overview

- Objective: Develop Electrolyzers That Can Be Convert CO_2 From Biorefineries To Produce Useful Products
- Save the cost of air capture



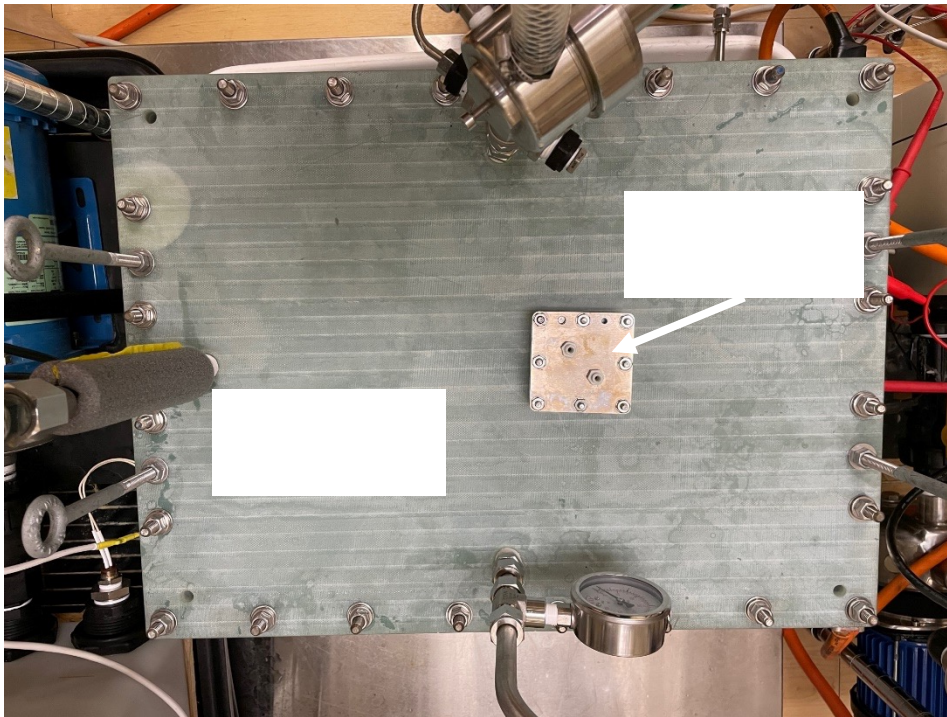
Project Objectives

- Move down the product development pathway



- Test with CO₂ from fermenter
- Understand how dilute/recycled CO₂ will affect performance

Size Comparison



1. Approach: Electrolyzer Scaling

- Design and build electrolyzer cells with 1000 cm^2 active area (The same size as in the proposed stacks)
 - Use CFD – one phase flow -to estimate flow distribution
 - Ignores 2 phase effects
 - Build the cells & run
 - Identify failure modes and repeat
- Milestones
 - Mid-project verification (100 hours @ 200 mA/cm^2 with 90% selectivity) (Met)
 - Project end (1000 hours @ 200 mA/cm^2 with 90% selectivity)

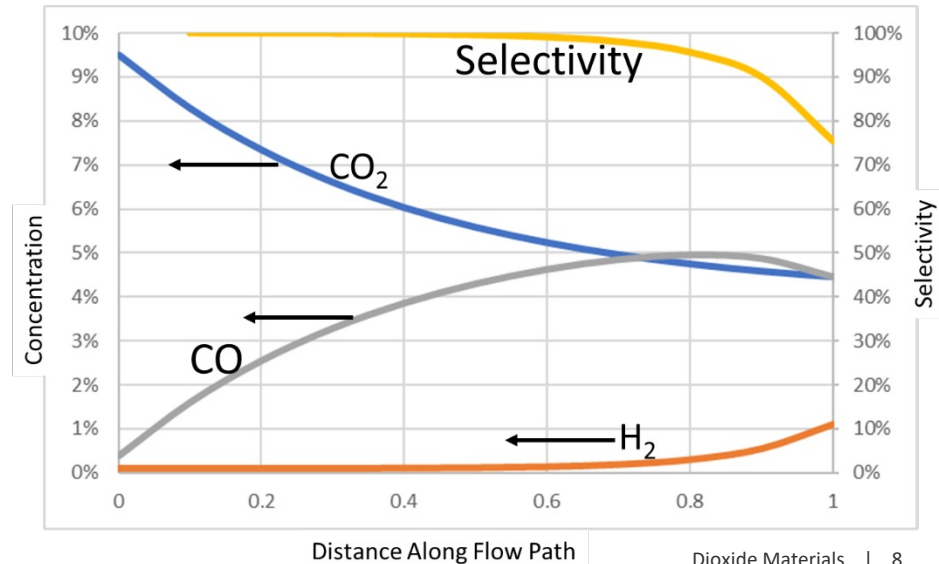
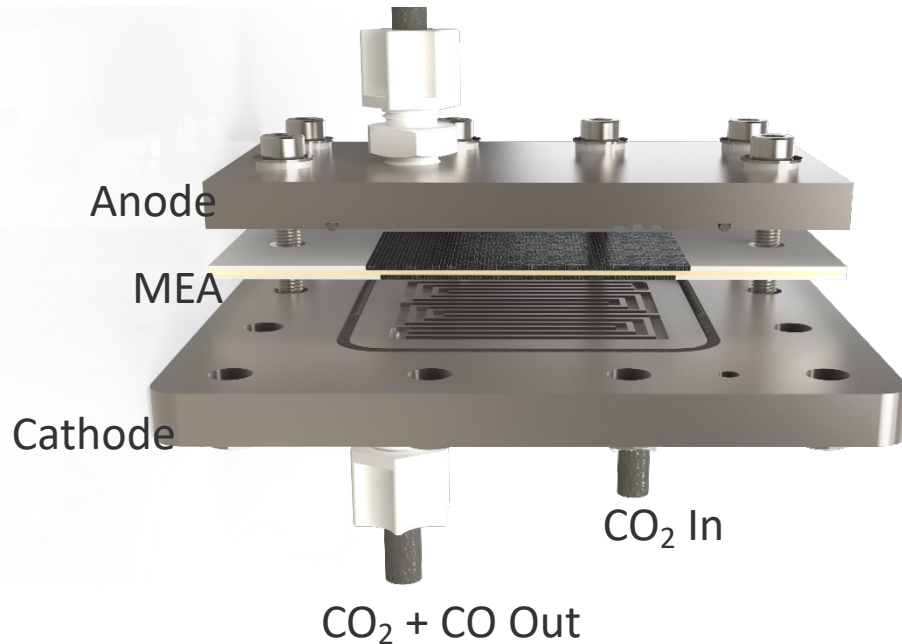
1. Approach: Electrolyzer Scaling

- Deconstructive Tests (suggested by verification team)
 - Load components from failed cells into small electrolyzer
 - Test modifications in small cells (e.g. stronger membranes) before moving to 1000 cm² cells

	Wet impact Strength, J, ASTM D3420
Standard membrane	0.056
Improved membrane	0.164
Grocery bag	0.1-0.15

1. Approach: Optimize Selectivity

- Concentrations drop as CO₂ and water are consumed
 - Cathode reaction: $\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{CO} + 2\text{OH}^-$
- What factors are limiting selectivity?

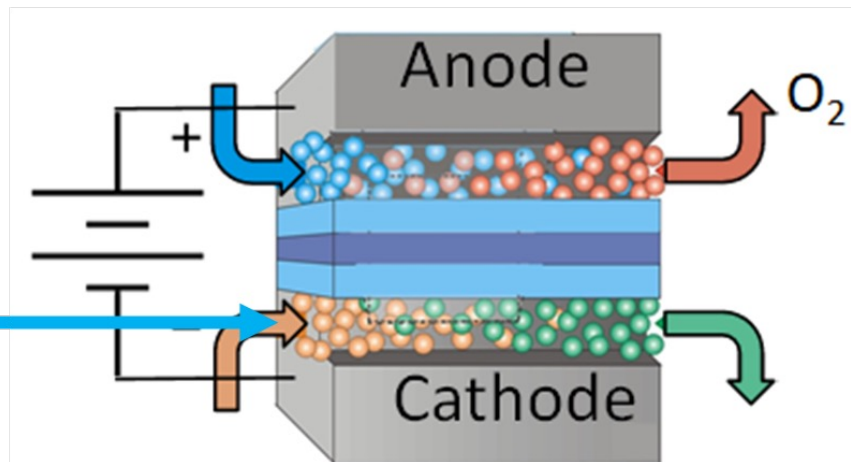
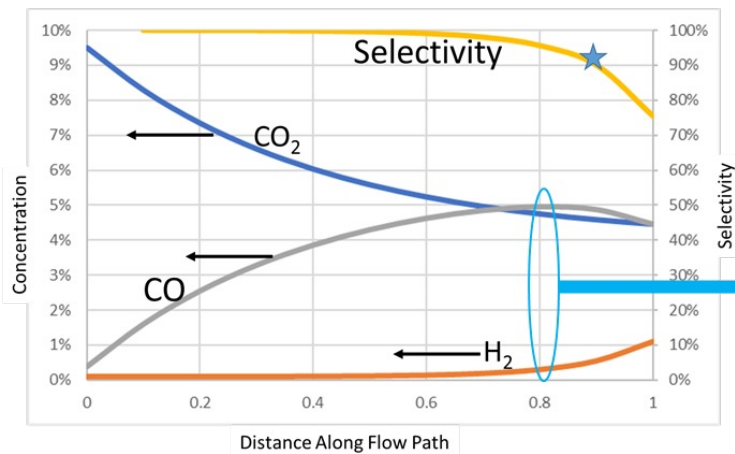


1. Approach: What Limits selectivity

Feed gas mixture with a concentration at each point on the curve

Flow rate high enough so concentration constant throughout the cell

Measure rate and selectivity as a function of concentration/humidity



Milestone: Paper describing the limiting factors

1 Approach: Use Results to Improve Performance

- BP2 work showed the catalyst layer structure has a significant effect on the selectivity
 - Originally proposed:
 - CT tomography to characterize the structure
 - Vary the preparation procedure to improve structure
 - New task
 - Capacitance measurements to characterize catalyst utilization
- BP3 – Milestone structure improvements to obtain 10, 20, 30, 40% increase in selectivity at reduced humidity

Approach: Testing On Fermenter Gas

- Original Plan: test 250 cm² cell on fermenter gas from Poet or ICM.
 - Requires huge volume of gas
 - Compression would change composition
- Revised plan: test large cell at the NREL process development unit (PDU)



TEA/LCA

- Develop low level TEA/LCA internally (Electrolyzer not system)
- Provide data to the NREL/ANL TEA/LCA team for more sophisticated results & system integration

Summary of The Approach

- Run a 1000 cm² cell, determine the failure modes and correct
- Learn the critical parameters that determine selectivity
- Provide data to NREL/ANL TEA/LCA team

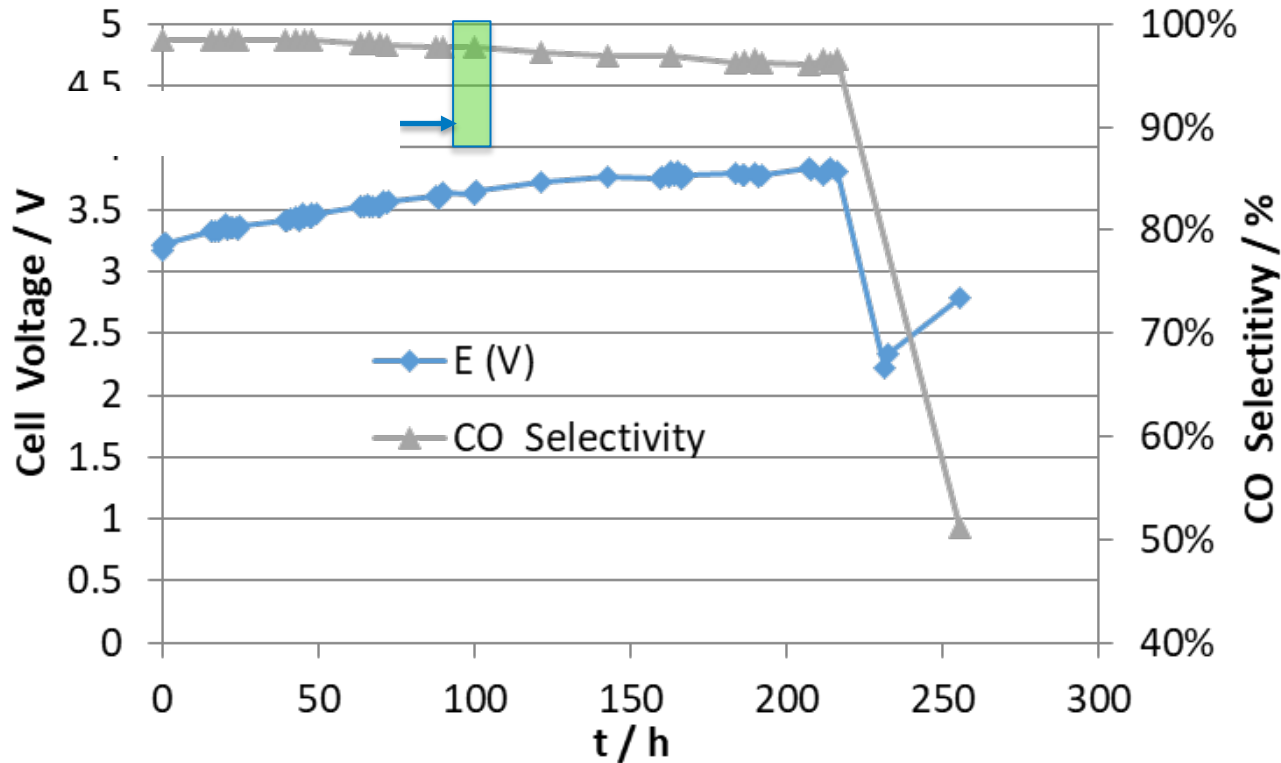
Next Progress and Outcomes

2. Progress and Outcomes

- Eight cell designs simulated, three built
- Met go/no-go milestone of $>200 \text{ mA/cm}^2$ for 100 hours with $>90\%$ selectivity



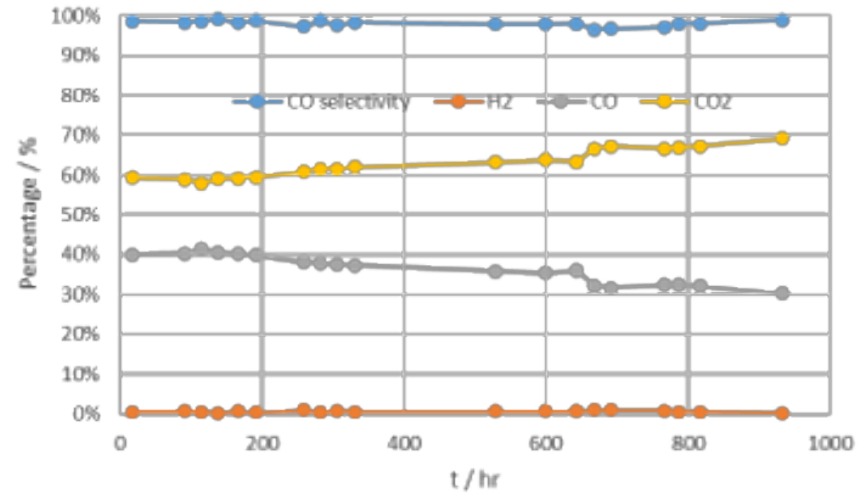
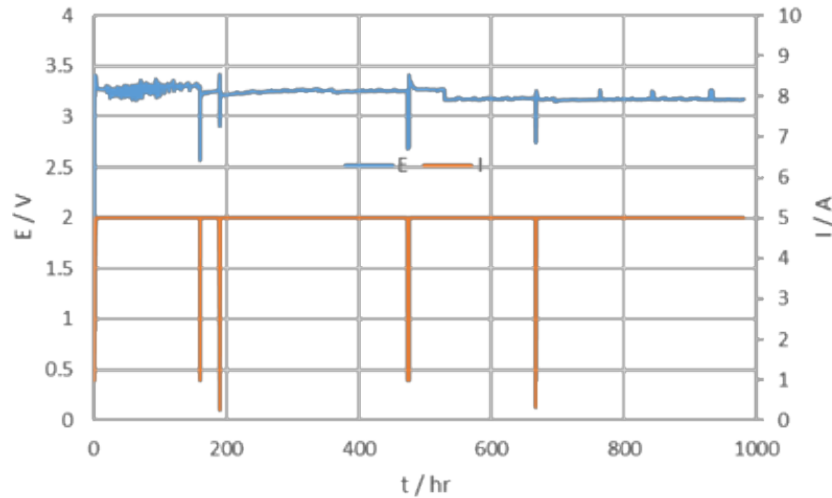
Run Meeting Go/No-Go Milestone



Meets go/no-go milestone: 100 hour performance, >90% selectivity

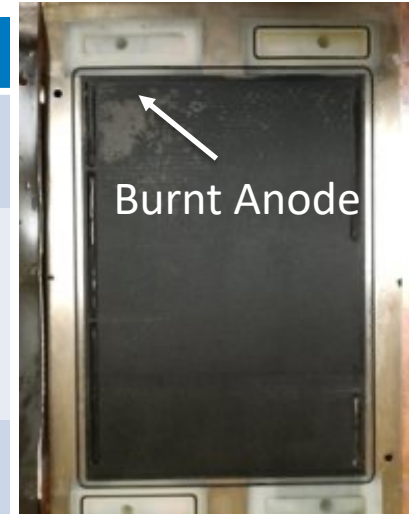
Test of MEA removed From Cell With Cracked GDL

- Cut out section of membrane from cell that had failed
- Mount in 25 cm² cell for testing – new GDL's



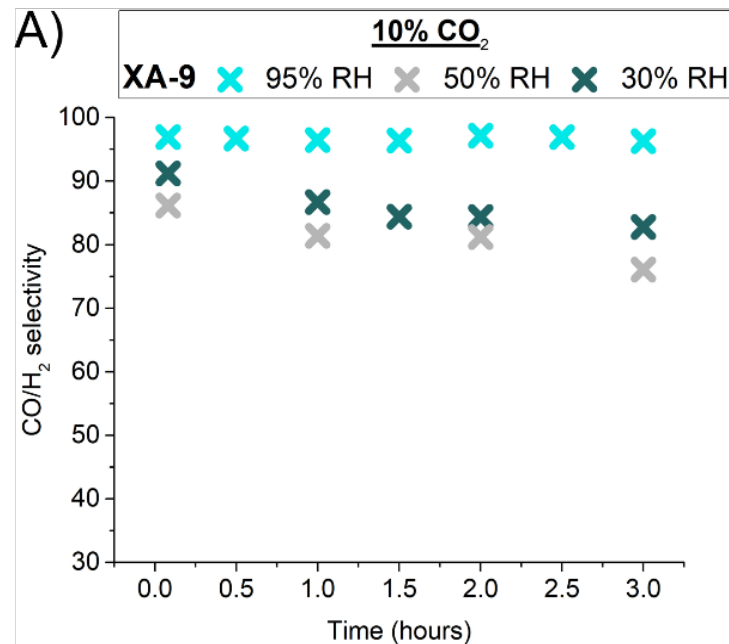
2. Main Failure Modes Due To Increased Size Identified

Failure Mode	Risk Mitigation
Thermal: Hot spots	<ul style="list-style-type: none">Design anode flow field so anolyte carries away heat ✓
Mechanical: Cathode GDL cracking & pushing through membrane	<ul style="list-style-type: none">Testing carbon cloth ✓Use conventional flow fields to better support the GDL ✓Strengthening the membranes ✓
Manufacturing defects: <ul style="list-style-type: none">Dust particle in membrane leading to failureConventional flowfield not Flat	<ul style="list-style-type: none">Manufacturing membrane in a clean environment ✓Membrane redesign ✓Identify high spots & polish
Supply Issues: Protruding fiber in GDL producing pinhole	
BOP: Power supply & pump failures	

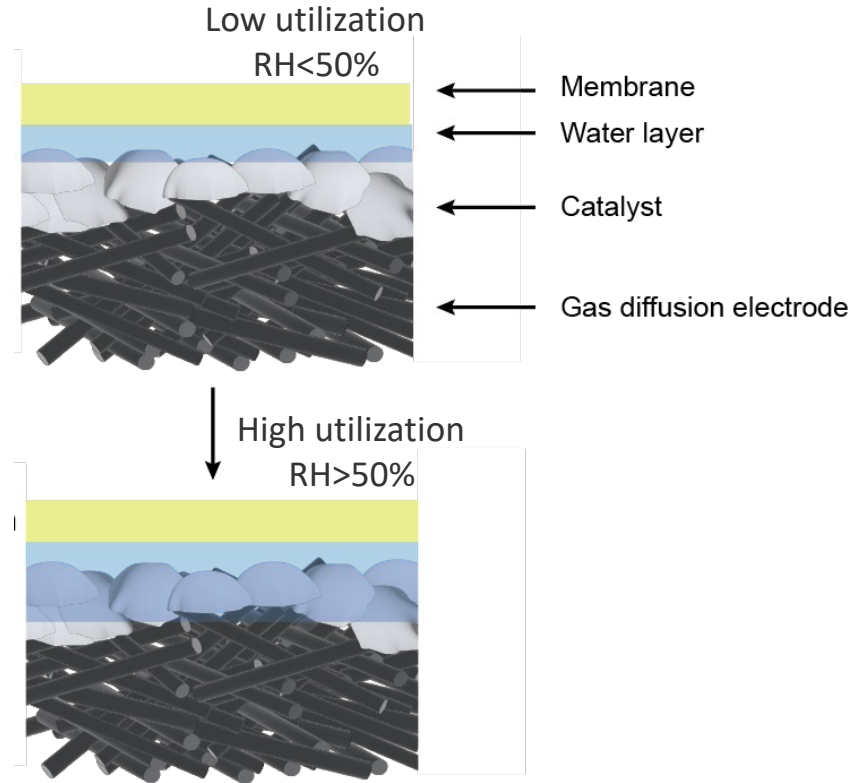


2. Progress and Outcomes: Selectivity Optimization

- Determined key parameters limiting selectivity
 - Humidity – can maintain selectivity above 90% down to 10% CO₂ if we keep humidity ~95% in cathode
 - Cathode reaction: $\text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{CO} + 2\text{OH}^-$
 - Catalyst layer structure: Need the full catalyst layer to be utilized
- Paper in preparation: Understanding the limits of Electrochemical conversion at low CO₂ concentrations



2. Progress and Outcomes: Selectivity Optimization

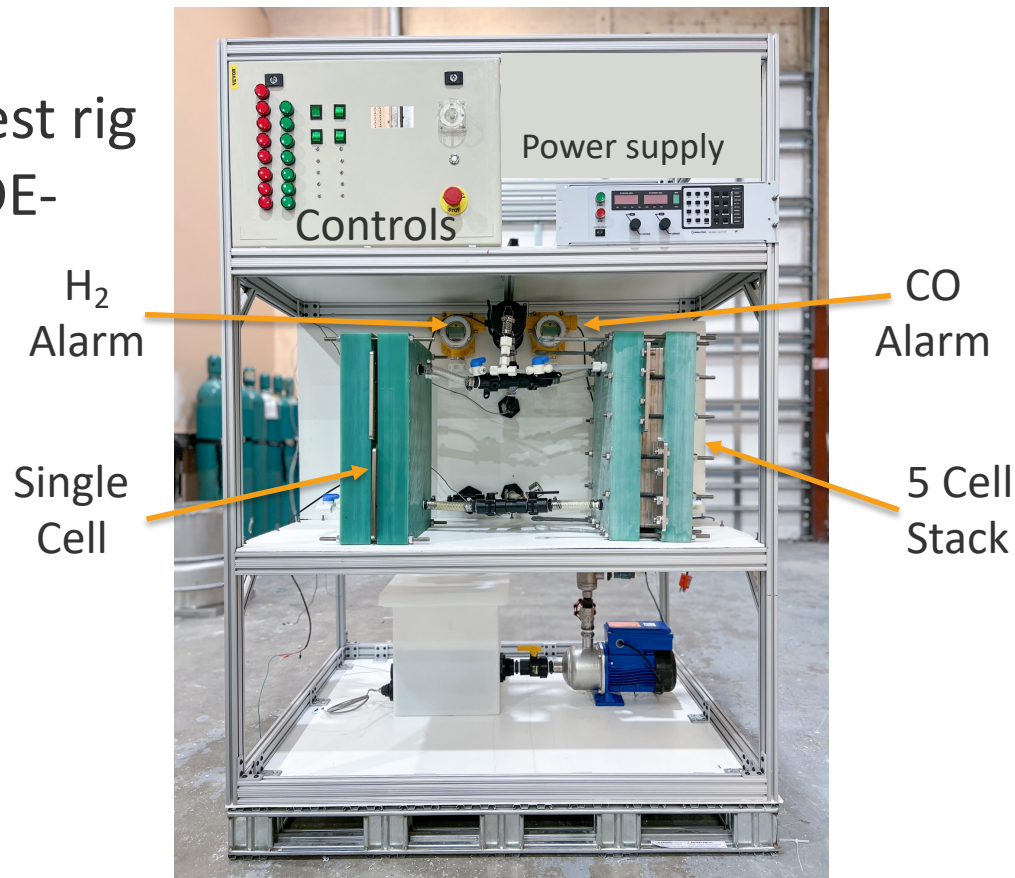


2. Progress and Outcomes: Selectivity Optimization

Selectivity Loss Mechanism	Risk Mitigation
Loss of humidity as H ₂ O is used up	<ul style="list-style-type: none">• Improve water transport in membrane• Dual cells with intermediate humidification ✓
Catalyst structure limits catalyst utilization	<ul style="list-style-type: none">• Modify layer preparation to improve structure

2. Progress and Outcomes Planning For PDU

- Continued developing test rig started under an SBIR (DE-SC0018540)

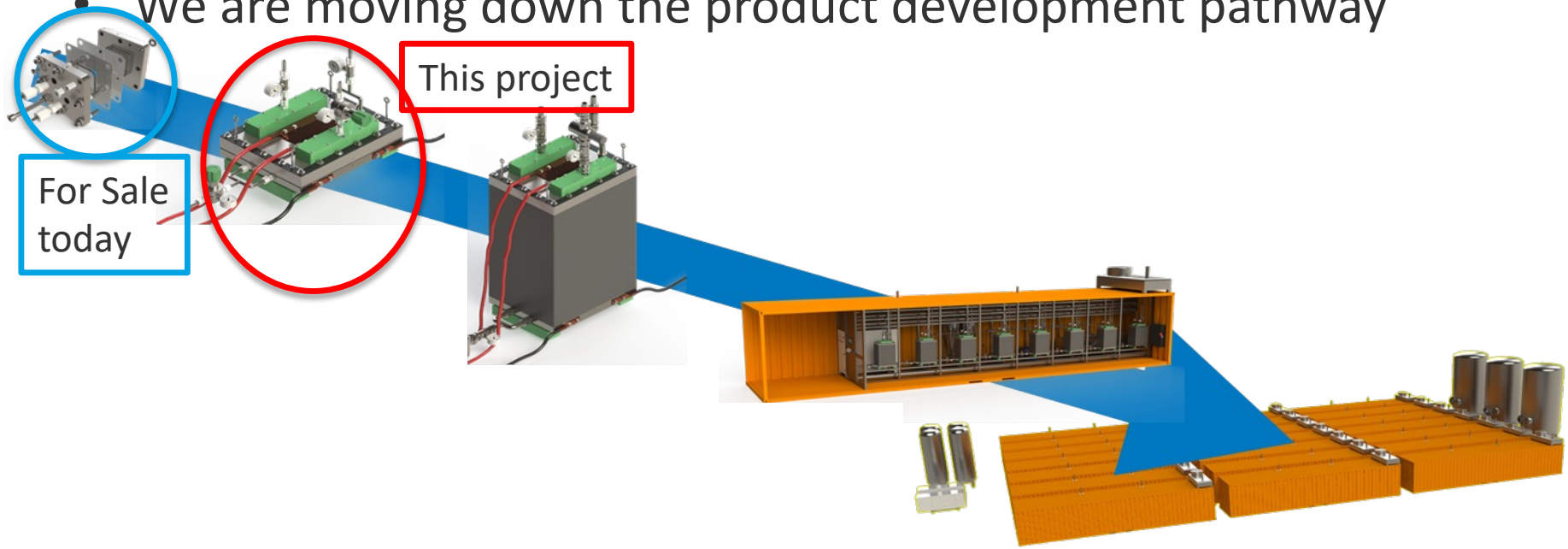


2. Progress and Outcomes: Preliminary TEA/LCA

- Need 3+ year lifetime before MEA replacement
- Need inexpensive electricity to make process economic
 - <\$0.03/kW in the US
 - <\$0.04/kW in the EU
 - <\$0.07/kW in China
- Need to power renewable/nuclear energy to reduce overall CO₂ emissions
 - Commercial scale plant needs 100+ MW electricity
- May need battery storage
 - Electrolyzer turns down easily if temperature maintained but downstream process cannot load follow

3: Impact

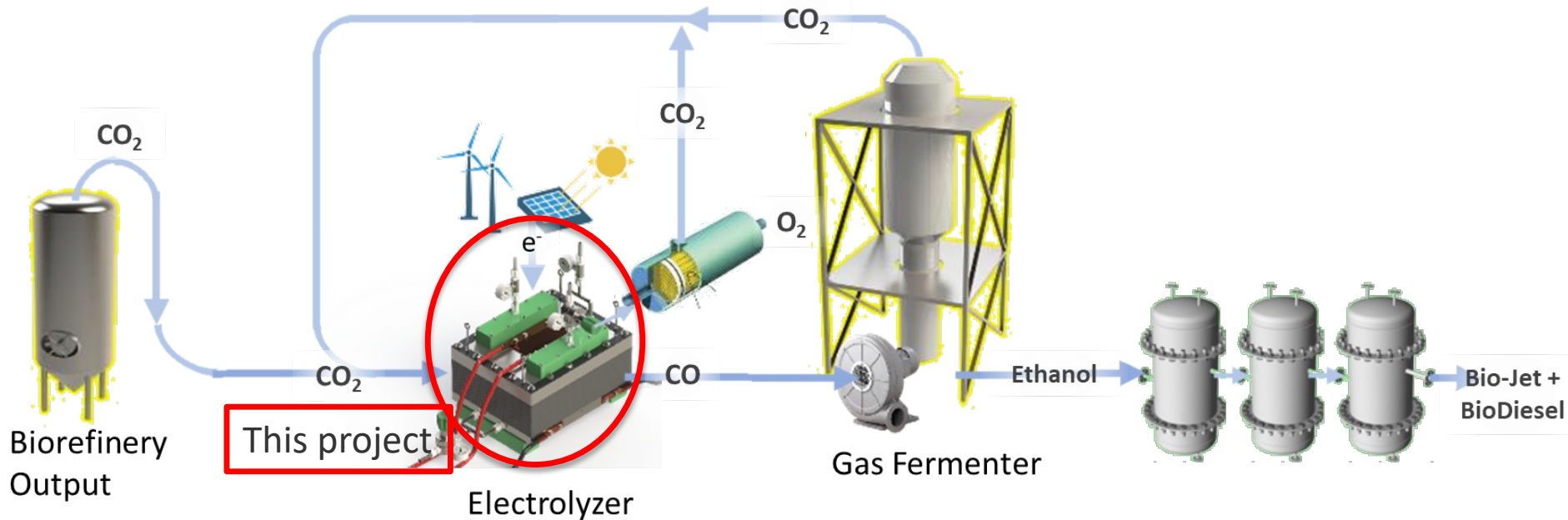
- We are moving down the product development pathway



performance and suggesting
improvements

3. Impact (Cont).

- Enabling a process to convert CO_2 from a biorefinery into SAF
- Save the cost of air capture
- Improving biorefinery carbon efficiency



Summary

- Cells with an active area of 1000 cm² feasible
- Lifetime limited by
 - Carbon paper defects
 - Dust
- Selectivity limited by
 - Catalyst layer structure
 - Water management
- 100 hours >90% selectivity demonstrated in 1000 cm² cell – project goal 1000 hours >90% selectivity

Quad Chart Overview

Project Goal

Scale Dioxide Materials electrolyzers to 1000 cm² size.

Improve selectivity

End of Project Milestone

Electrolyzer cell with an active area above 750 cm² operating for 1000 hours with a selectivity above 90%

Funding Mechanism

FY2020 DE-FOA-0002203

Project Partners*

- NREL (\$600,000)
- ANL (\$75,000)

	FY22 Costed	Total Award
DOE Funding		
Project Cost Share*		

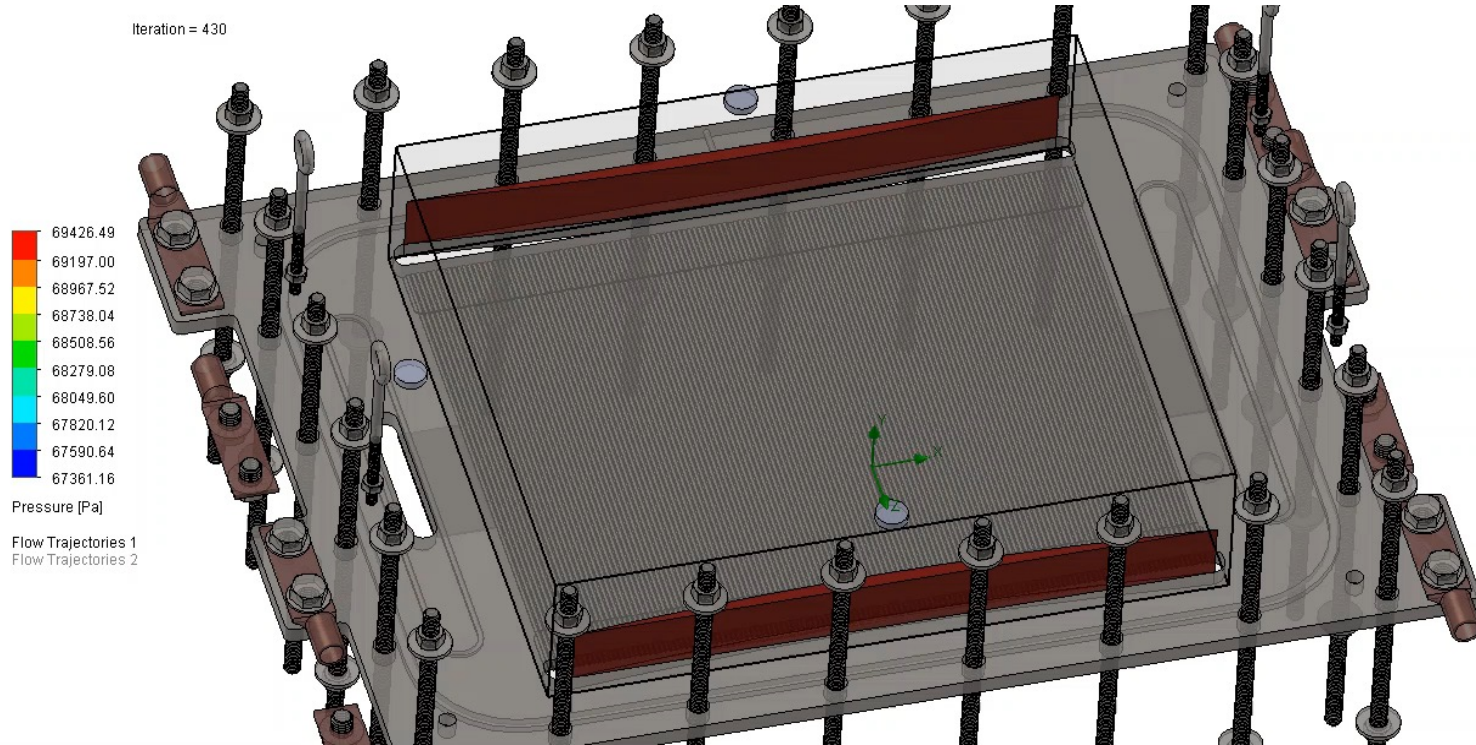
TRL at Project Start: 2 for 1000 cm² cell
TRL at Project End: 5

dioxidematerials.com

This work was supported by the Department of Energy under contract DE-EE0009286. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

Additional Slides

Movie of Simulation To Understand Dead spots

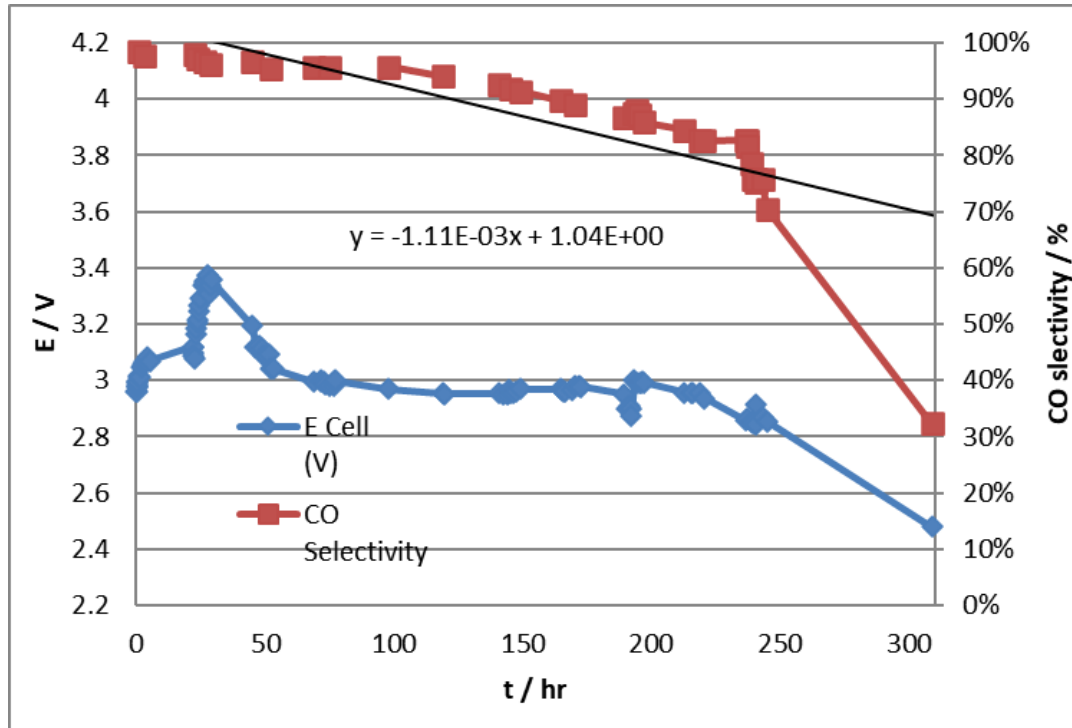


Many dead zones

First test of new flowfields to support GDL

Membrane with dust particles. Dust was from remodeling at new facility

- No issues with GDL



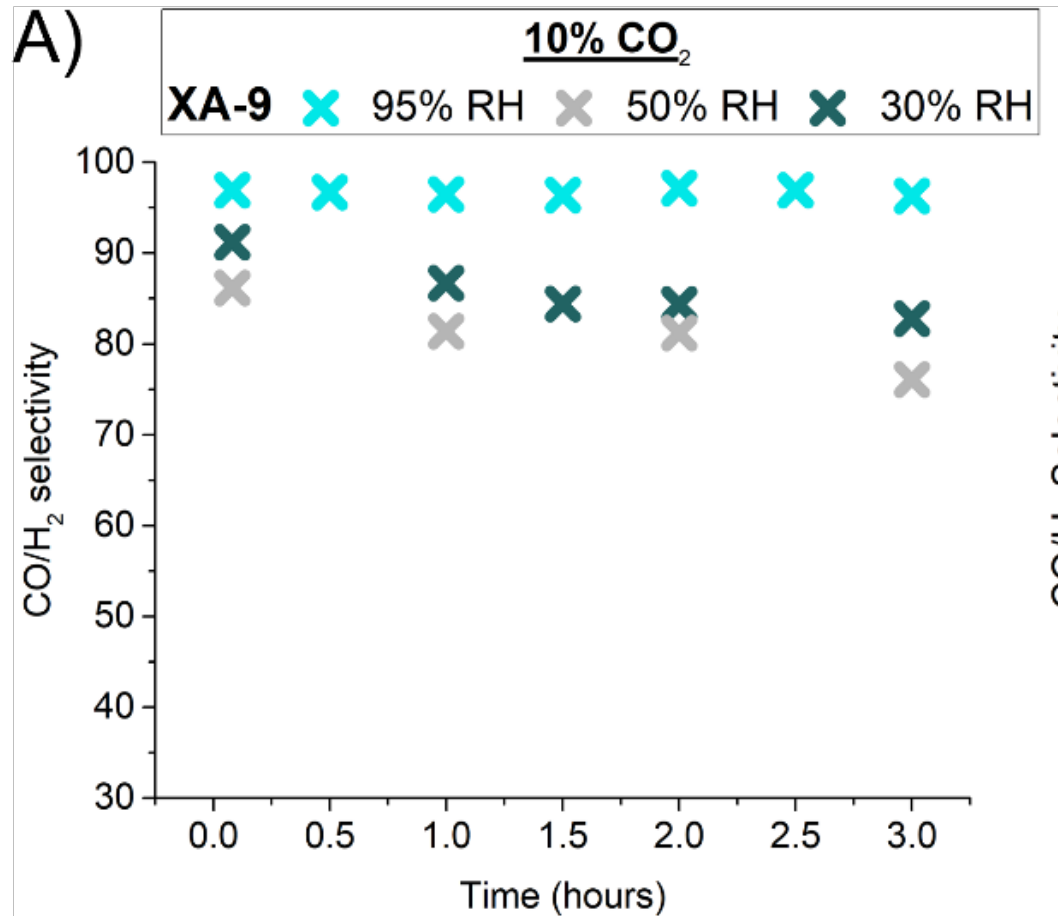
Membrane Impact Strength Improvement

	Impact Strength, J, ASTM D3420
Standard membrane	0.056
Improved membrane	0.164
Grocery bag	0.1-0.15



Device measures energy needed to punch a hole in the membrane

Selectivity Data



BP1 Milestones

	2.1 Create 30 cm membranes	25-Nov-21
2.1.ML.1	Membranes that are 28+ cm wide and at 40+ cm long	25-Nov-21
	2.2 Anode Flowfields	28-Oct-21
2.2.ML.1	Simulations indicate equal flows	28-Oct-21
	2.3 Assemble with balance of plant	17-Mar-22
2.3.ML.1	Temperature controlled	17-Mar-22
	2.4 Electrolyzer operation	18-Oct-22
2.4.ML.1	200 mA/cm ² achieved in a cell with an active area of at least 750 cm ² for ≥24 continuous hours	22-Apr-22
2.4.ML.2	200 mA/cm ² achieved in a cell with an active area of at least 750 cm ² for ≥100 continuous hours	20-Jun-22
2.4.ML.3	200 mA/cm ² at ≥ 80% selectivity to CO achieved in a cell with an active area of at least 750 cm ² for ≥100 continuous hours	19-Aug-22
2.4.ML.4	200 mA/cm ² @ > 90% selectivity, active area ≥750 cm ² for ≥100 continuous hours	18-Oct-22
	3.3 Test alternate ionomers/catalysts	25-Jan-23
3.1.1	base case	24-Nov-21
3.1.ML.1	Determine lowest CO concentration where 90% selectivity can be obtained as a function of Temperature and humidity	24-Nov-21
3.1.2	gold catalyst	17-Feb-22
3.1.ML.2	Determine lowest CO concentration where 90% selectivity can be obtained as a function of Temperature and humidity	18-Feb-22
3.1.3	Alternate ionomer 1	13-May-21
3.1.ML.3	Determine lowest CO concentration where 90% selectivity can be obtained as a function of Temperature and humidity	16-May-22
3.1.4	alternate ionomer 2	4-Aug-22
3.1.ML.4	Determine lowest CO concentration where 90% selectivity can be obtained as a function of Temperature and humidity	5-Aug-22
	4.4 Papers and conference meetings	6-Apr-23
4.ML.1	Paper presented at BETO AMR	6-Apr-23

BP2 Milestones

5.1	250 hour tests	19-Jan-23
5.1.ML.1	200 mA/cm ² @ > 90% selectivity, active area ≥750 cm ² for ≥250 continuous hours	19-Apr-23
5.2	500 hr tests	20-Aug-23
5,2.ML1	200 mA/cm ² @ > 90% selectivity, active area ≥750 cm ² for ≥500 continuous hours	20-Aug-23
5.3	1000 hr tests	29-Jan-24
5.3.ML.1	Milestone: 200 ma/cm ² @ > 90% sel, 1000 hr	29-Jan-24
	66 ionomer optimization	14-Nov-23
6.1	Tests of alternate ionomers	7-Feb-23
6.1.ML.1	Milestone: 10% improvement compared to task 3	7-Feb-23
6.1.ML.2	Milestone: 20% improvement compared to task 3	30-May-23
6.2	Tests in commercial cells	25-Jul-23
6.2.ML.1	Milestone: 20% improvement compared to task 3	25-Jul-23
6.3	Nano-Computed Tomography	12-Dec-23
6.3.ML.1	Nano-Computed Tomography on catalyst from task 3	17-Feb-23
6.3.ML.2	Nano-Computed Tomography on catalyst from 6.1.1	25-Jul-23
6.3.ML.3	Nano-Computed Tomography on catalyst from 6.1.2	12-Dec-23
	77 structural improvements	18-Jan-24
7.1	Tests of alternate structures	18-Jan-24
7.1.ML.1	Milestone: 10% improvement compared to task 6	22-Aug-23
7.1.ML.2	Milestone: 20% improvement compared to task 6	14-Nov-23
7.2	Tests in commercial cells	18-Jan-24
7.2.ML.1	Milestone: 20% improvement compared to task 6	18-Jan-24
	88 Integration with Fermenter	17-Jan-24
8.1	Integration with fermenter	19-Dec-23
8.1.ML.1	20% CO converted to ethanol	30-Nov-23
8.1.ML.2	40% CO converted to ethanol	19-Dec-23
	8.2 Operation of gas from a biorefinery	19-Dec-23
8.2.ML.1	Milestone: ethanol produced	19-Dec-23

Publications

1. Henckel, D.A., Rajana, S., Liu, Z., Resch, M., Masel, R. I., Neyerlin, K.C., Enabling high selectivity for CO₂ to CO conversion at low CO₂ partial pressures (In Preparation)

Commercialization

- Dioxide Materials is planning to offer new stronger membranes shortly
 - Now developing SOP for commercial production
- Dioxide Materials has been selling small electrolyzers since 2018
 - Will incorporate stronger membranes shortly